

Chlorine Dioxide Residual

An aspect of papermaking undergoing tremendous change is pulp bleaching. For chemical pulp bleaching there is a definite trend to either eliminate or significantly reduce chlorine use. Increasingly higher substitutions of chlorine dioxide in the first bleaching stage are common. As a result of this increased use of chlorine dioxide, many mills are dioxide limited.

Additional chlorine dioxide generating capacity requires capital expenditure. However, more efficient use of the current amount of chlorine dioxide produced could allow for a higher chlorine dioxide substitution ratio in the first stage without compromising final pulp brightness. With on-line residual chlorine dioxide analysis using the AMETEK Model 4000 Photometric Analyzer, it is possible to use the minimum amount of chlorine to achieve the target residual level. It is no longer necessary to use more chlorine dioxide than is required to ensure that the target residual level is maintained. Lab testing for residual levels is no longer necessary and the incidence of dips in chlorine dioxide residual level below the target value is removed.

When the concentrations of bleach chemicals are known and

the minimum amounts are used, there are a number of benefits achieved: reduced environmental impact, reduced effluent load, and lastly, pulp of higher and more consistent quality is produced. Continuous, on-line residual analysis with the 4000 provides a means to use chlorine dioxide most efficiently and to increase the uniformity and overall brightness level of pulp.

D₁ and D₂ Stage Control Strategies

In the interest of pulp quality and bleaching economics, it is important to control the chemical dosage in all bleaching stages. The control strategy for each stage is comprised of both long and short term strategies due to the long retention times in the bleaching towers. For the dioxide stages, the long term strategy has generally been to reach a 75 to 80 brightness in the D₁ stage and a brightness above 90 for the D₂ stage. Short term control is then achieved through measurement of the chlorine dioxide residual in the pre-tower filtrate. Residual targets for the D₁ stage, for example, are then updated to reflect the long term trends in the D₁ stage brightness and E1 K number.

Residual control is important for both the D₁ and D₂ stages.

A residual must be maintained throughout the stage to prevent brightness reversion of the pulp caused by the (50 to 70°C) temperatures in the tower. In addition, finite residual levels promote pulp cleanliness by improving the bleaching of shives. If the final product is market Kraft pulp for example, cleanliness is especially important for production of the highest quality grades. By maintaining the residual level throughout the stage in order to eliminate brightness reversion and to improve pulp cleanliness, a high brightness pulp is achieved as a result.

Continuous monitoring of the residual level permits feedback control to compensate for variations in the chlorine dioxide demand. This eliminates the need to maintain excessively high residual levels to allow for this variability. Control of the chlorine dioxide bleaching stages based on a continuous residual measurement would, therefore, be of great value. Continuous analysis of the residual in closed-loop control to regulate the chlorine dioxide injection would permit significant savings in chemicals by allowing the stage to be run at the target residual level rather than above it.

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The Residual Measurement

Chlorine dioxide exhibits a strong absorbance in the uv-visible spectrum which suggests measurement of the residual via spectrophotometry. It is more strongly absorbing in this region than all other bleach plant oxidants. At the measuring wavelength selected for the model 4000, the absorbance of chlorine dioxide is not affected by either chlorine or sodium chlorite which may be present.

Chlorite might be expected in the D₁ stage if the pH rises above 4.0. Under these conditions, significant concentrations of chlorite can develop since the chlorine dioxide only partially reacts with the pulp while the chlorite formed is unreactive. Neither typical mill titrimetric methods

nor polarographic sensors can differentiate chlorine dioxide and chlorite under the high pH conditions. Even with a high ratio of chlorite to chlorine dioxide (1/1 molar ratio), the model 4000 measures only the absorbance due to chlorine dioxide.

In addition to providing an accurate measurement of chlorine dioxide at a high pH, the residual measurement should be insensitive to changes in pH. Variations in pH are common during pulp bleaching due to fluctuations in the washing efficiency of the extraction stage directly before it. The absorbance of chlorine dioxide is independent of pH since it is a free radical. Measurement of the residual with the model 4000 is thus, independent of pH.

Mill Experience

A model 4000 was installed in November 1986 to monitor and control chlorine dioxide residual on a D₂ stage. During that time, the incidence of off-grade low brightness pulp has been reduced from 1.9 percent of the total production down to 0.4 percent. The D₂ stage brightness levels have increased and the monthly average standard deviations of the final pulp brightness levels have decreased. Improved control of the D₂ stage residual has decreased the incidence of over-bleaching. Not only does over-bleaching waste chlorine dioxide, but it also causes high washer and vat residuals which off-gas into the work environment. The analyzer has proved reliable and has contributed to significant savings. The mill has recently installed two more model 4000s as residual controls, one on a D₁ stage and another on a D₂ stage.



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ClO₂Residual (06/05/07)

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